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15th Annual Non-Point Source Water Quality Monitoring Results Workshop

Optical Dissolved Oxygen Sensors

Maximizing Accuracy and Precision While Minimizing Maintenance

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In-Situ and EDS partnership

- In-Situ Inc., Headquartered in Fort Collins, CO
  - founded in 1978 and manufactures equipment for Water Quality and Water Level monitoring applications

Troll Multiparameter Water Quality Sondes

MiniTroll Water Level and Temperature Loggers

Hermit Dataloggers

In-Situ and EDS partnership

ELECTRONIC DATA SOLUTIONS

- EDS – founded in 1986, Based in Jerome, ID
- Specialize in natural resource applications including forestry and range management, fish and wildlife management, agriculture and aquaculture management and water resource management in the western United States

- Hand held field computers
- Water quality instrumentation
- Ground water monitoring equipment
- GPS receivers for mapping applications
- GPS vehicle tracking systems
- Laser rangefinders
- GIS Software
- Water level monitoring and control systems
- Database, graphing and analysis software

www.electdata.com

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Optical DO sensors…What's the buzz all about?

- Solid State Construction
- Rely on Dynamic Fluorescence Quenching
- Lifetime-based fluorescence measurement
- NOT based on electrochemical reactions
- A new way of thinking about DO measurement
- Eliminate problems inherent to older DO sensor technologies

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Who spearheaded the development of Optical DO sensors??? YOU!!!

During multiple customer and end-user interviews the overwhelming concern expressed by industry professionals was <u>problems with, and lack of confidence in, their existing DO instrumentation and results!</u> WHY?

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Electrochemical Sensors (Clark, Galvanic) are affected by several factors:

1. Temperature
2. Flow/Stirring
3. Degraded membranes and electrolyte
4. Proper maintenance and calibration
5. Storage and sensor conditioning

- POOR QUALITY DATA - Without frequent calibration and maintenance the Electrochemical sensors are difficult to use for accurate and dependable measurement.

- HIGH COST OF OWNERSHIP - Many deployments require a site visit every two weeks or more often to calibrate and replace failed sensors.

Time, Money, & Hassle!

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ALLIANCE FOR COASTAL TECHNOLOGIES

www.actonline.ws

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION U.S. DEPARTMENT OF COMMERCE NOAA

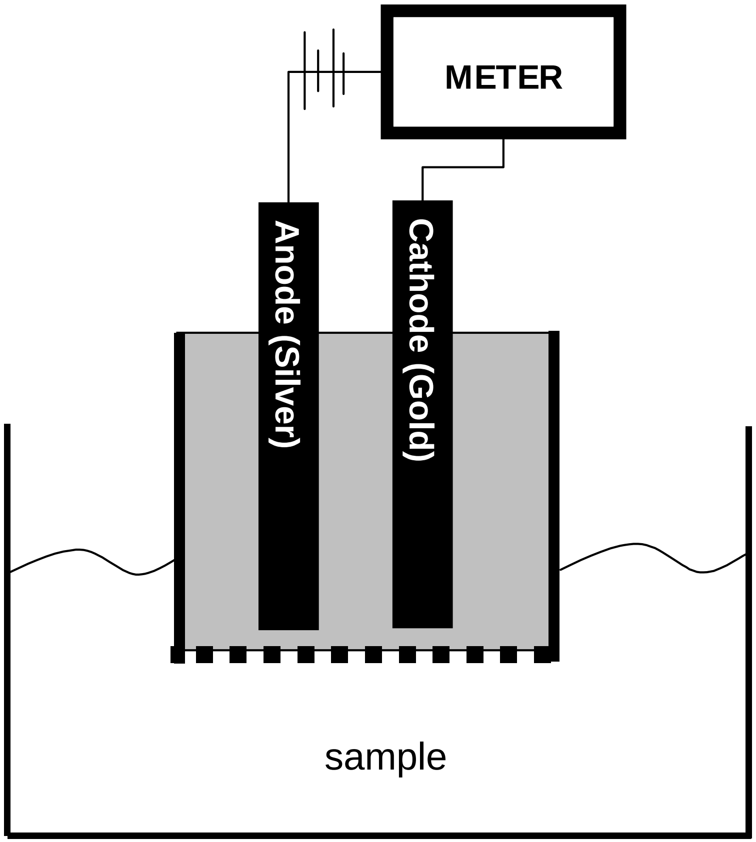
Variable	Galvanic	Polarographic Steady State	Polarographic Pulsed	Optical Steady State	Optical Life
Flow dependence	Low	High	Low	None	None
High pressure hysteresis (over 500 m)	Yes	Yes	Yes	No	No
Response time (to 90%)*	Slow	Medium	Medium	Fast	Fast
Range (0-2008)	Yes	Yes	Yes	Yes	Yes
low end (0-1 ppm)	+	+	+	++	++
high end (20 ppm)	++	++	++	+	+
Long term stability	+	+	+	++	++
Frequency of maintenance	High	High	High	Low	Low
Calibration					
zero point required	No	No	No	No	No
factory or labor atory	F	F/L	F/L	F	F
difficulty	N/A	Medium	Medium	N/A	N/A

*Slow ≈ 7 minutes, Medium < 1 to 3 minutes, Fast < 1 minute

++ indicates better performance than +

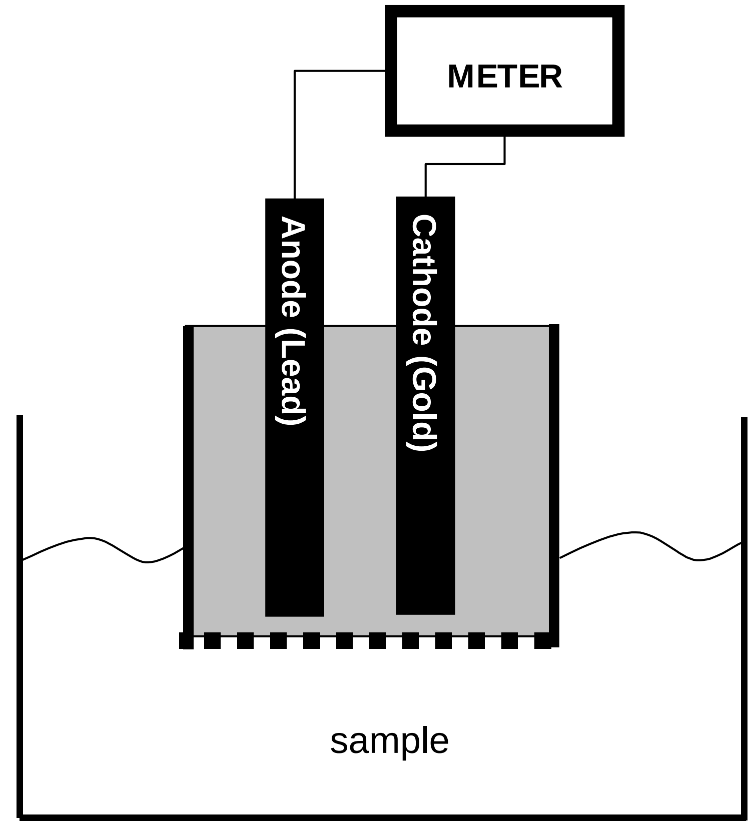
State of Technology in the Development and Application of Dissolved Oxygen Sensors, **Alliance for Coastal Technologies (ACT) Workshop Proceedings, Savannah, Georgia, January 2004; University of Maryland Technical Report series No. TS-444-04-CBL, p. 11.**

Polarographic



Voltage potential generated by meter

Galvanic



Voltage potential supplied by electrodes

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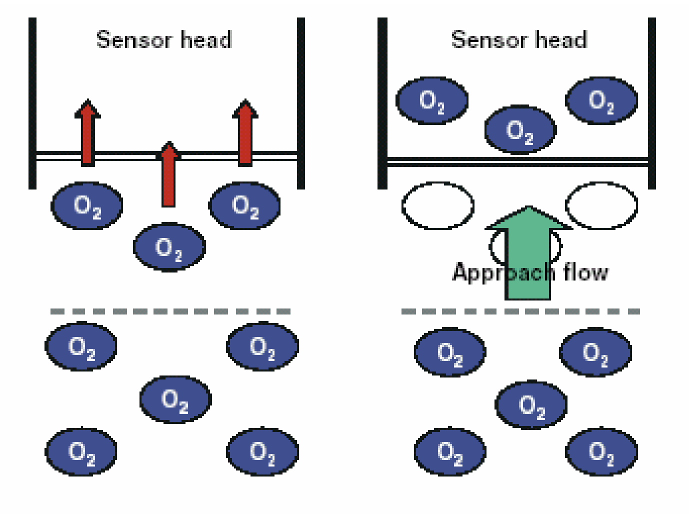
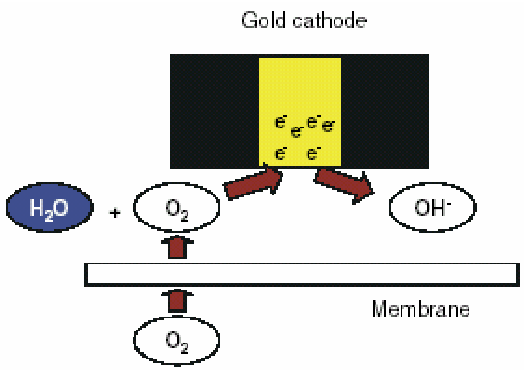
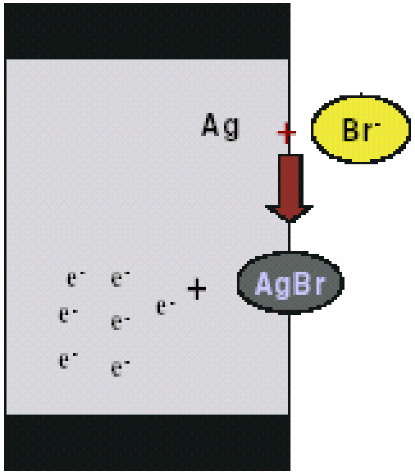
Electrochemical reaction in a Polarographic DO sensor





$$O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-$$

Silver anode



$$Ag \longrightarrow Ag^+ + e^-$$

$$Ag^+ + Br^- \longrightarrow AgBr\downarrow$$

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Key Components of Optical DO Sensors

Titanium

Depths to 6000 m

Delrin®

Depths to 2000 m

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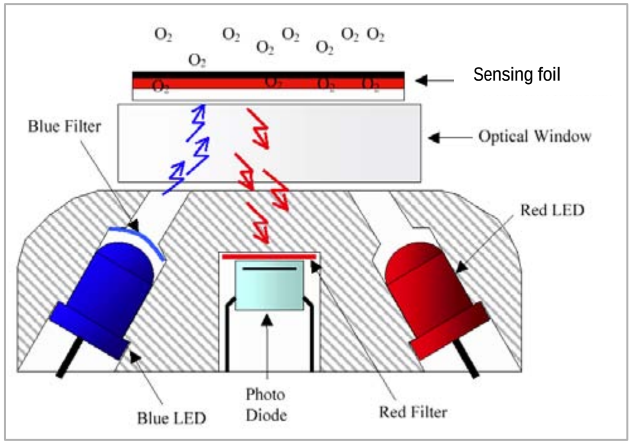
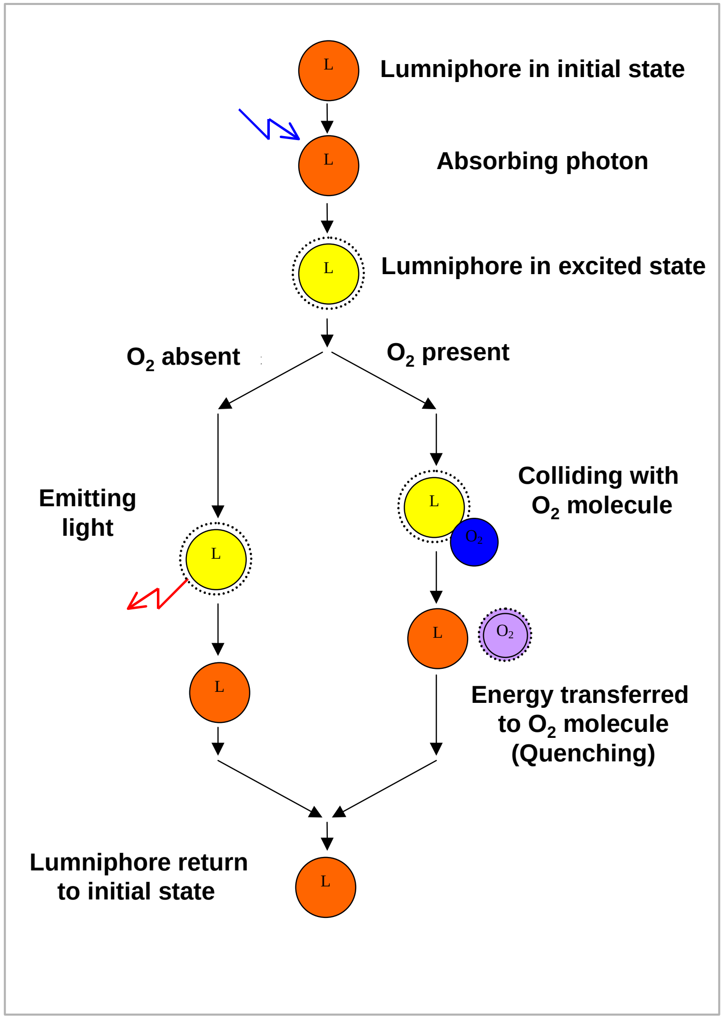
Optical DO Theory

- The sensing element (luminophore) is activated, or excited when illuminated with a blue light
- When activated, the sensor emits red light in an amount inversely proportional to the amount of oxygen present in the water
- There is also a **time delay** between the emission of blue and fluoresced red light. The amount of delay is dependent on the amount of oxygen present.
- This time delay results in a **phase shift** between the fluoresced red light and reference wave form emitted by the red LED.

All of the optics and electronics are solid-state with no moving parts





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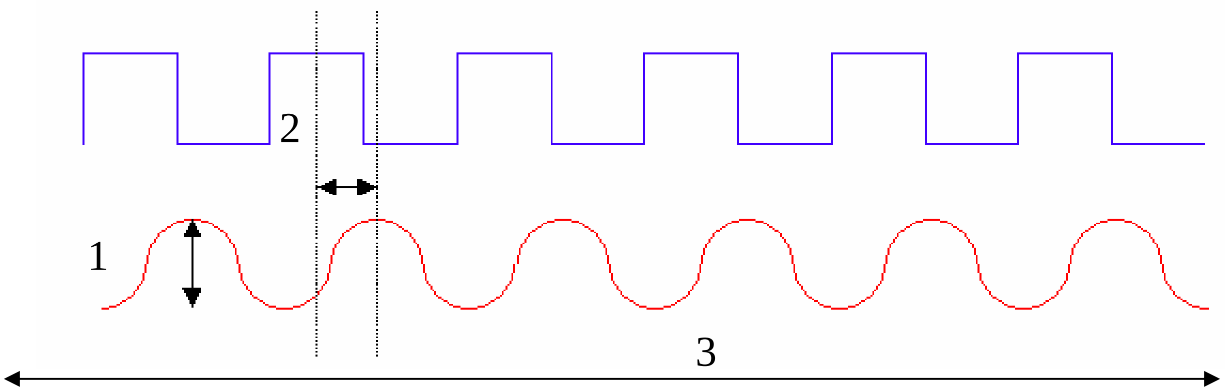
3 ways to measure -



1. **Magnitude** – Potential for interference from ambient light. Peak height degrades over time as lumiphore ages. Requires more frequent calibrations

2. **Time Domain** – Subject to errors due to problems with peak detection. Signal to noise ratio limits range. Better results than magnitude-based

3. **Phase Domain** – Lock-in amplifier determines phase angle based on entire signal and reference wave forms. Magnitude is not important, wider operating range. Best precision and accuracy.

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Features of Optical Dissolved Oxygen Sensors

- No membranes/no electrolyte
- 5 years/5 Million readings before lumiphore is exhausted
- Up to 1 year between calibrations
- Minimal maintenance/no hazardous sensor cleaning solutions
- No sample flow requirements
- Fast and stable response
- Resist biofouling - Suited for long-term deployments
- Little or no sensor drift over several months
- Excellent performance in anoxic conditions—full sensor response at 0 ppm
- Not 'poisoned' by Sulfides
- Accurate results up to and above 200% saturation
- Not subject to 'thermal shocking'
- No cross sensitivity to: H_2S, pH, CO_2, NH_3, SO_4^{2-}, Cl^-, Cl_2, ClO_2, MeOH, EtOH, various ionic species

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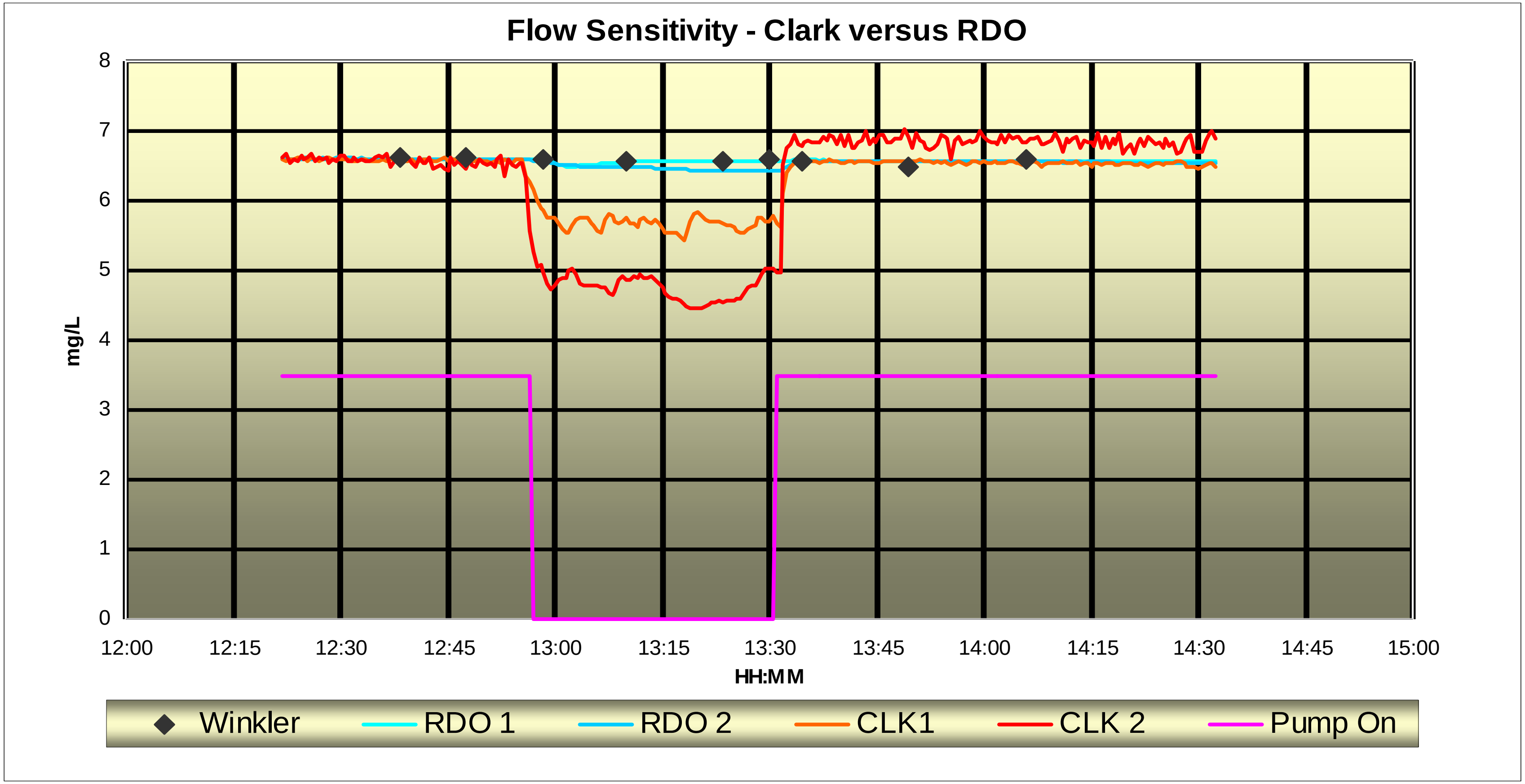
Comparative test showing effects of stirring between Optical DO Sensor and Clark Cell Polarographic Sensor



Clark cell technology required flow to achieve accurate results

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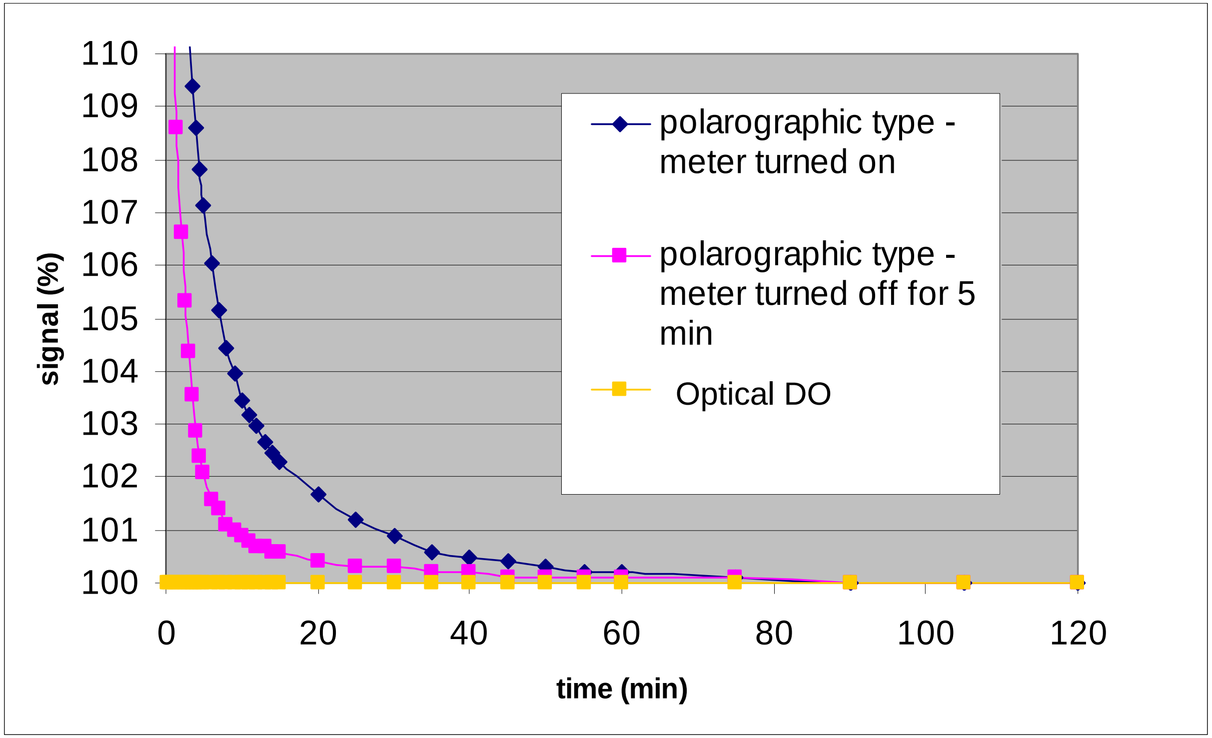
Comparison of probe polarization (warm-up) times



Curve 1 - Polarographic probe, initial warm up time

Curve 2 - Polarographic probe, turned off for 5 min. after initial warm up, then back on

Curve 3 - Optical DO sensor (no warm-up required)

ACT DO sensor validation program – partner sites

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UMD/Chesapeake Biological Lab	Maryland
- Headquarters and a field site	
CILER/University of Michigan	Michigan
- Field site and lab facility	
GoMOOS/University of Maine	Maine
Moss Landing Marine Lab/Cal State	California
Skidaway Institute of Oceanography	Georgia
University of Hawaii	Hawaii
University of South Florida	Florida

Good representation of various geography and coastal environments

Table 2. lists the basic test site descriptions and field conditions during testing.

ACT Partner Test Site	Basic Characterization	Range in Water Temperature (°C)	Range in Salinity (ppt)
Bayboro Harbor, FL	An estuary in the southwestern region of Tampa Bay	26.4 – 31.8	4.4 – 24.2
Belleville Lake, MI	A freshwater impoundment on the Huron River	22.5 – 27.1	0.0 – 0.1
Kaneohe Bay Reef, HI	A high energy barrier coral barrier reef	25.1 – 28.7	34.4 – 34.9
Moss Landing, CA	An estuarine tributary of the Salinas River in Monterey Bay	14.0 – 17.3	30.9 – 33.5
Skidaway Island, GA	A subtropical estuary on the Skidaway River on the western shore of Skidaway Island	23.8 – 29.8	18.4 – 30.9
Solomons, MD	An estuary at the mouth of the Patuxent River in the Chesapeake Bay	24.3 – 28.1	9.8 – 12.0
Walpole, ME	A tide dominated embayment/ Damariscotta River estuary	13.1 – 18.7	29.6 – 31.2

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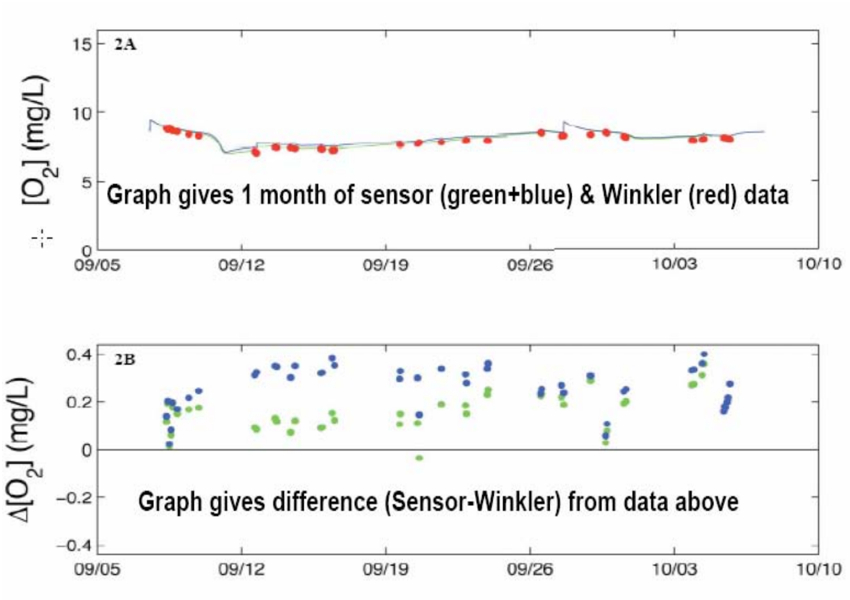
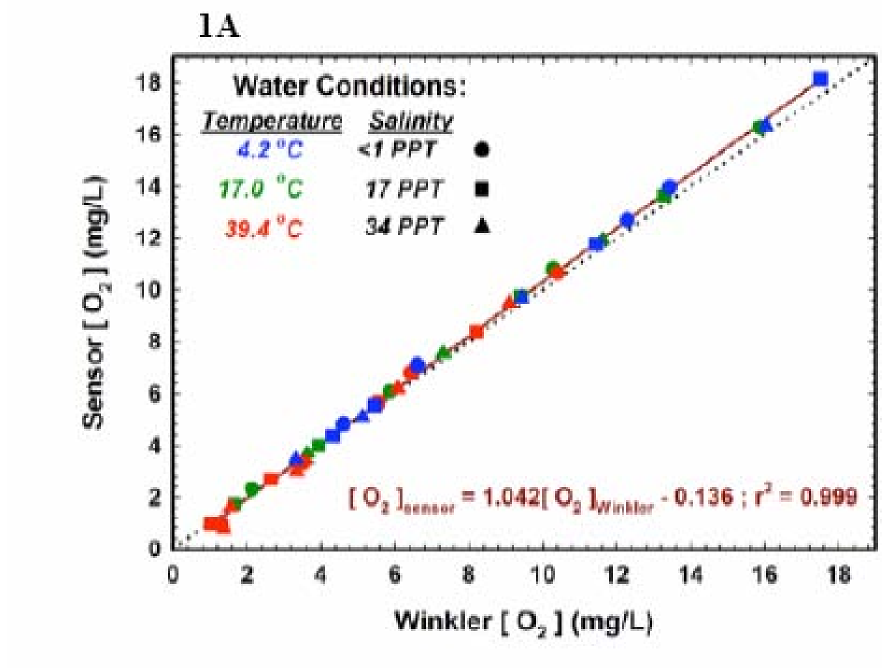
Optical DO Sensor drift and accuracy under lab conditions





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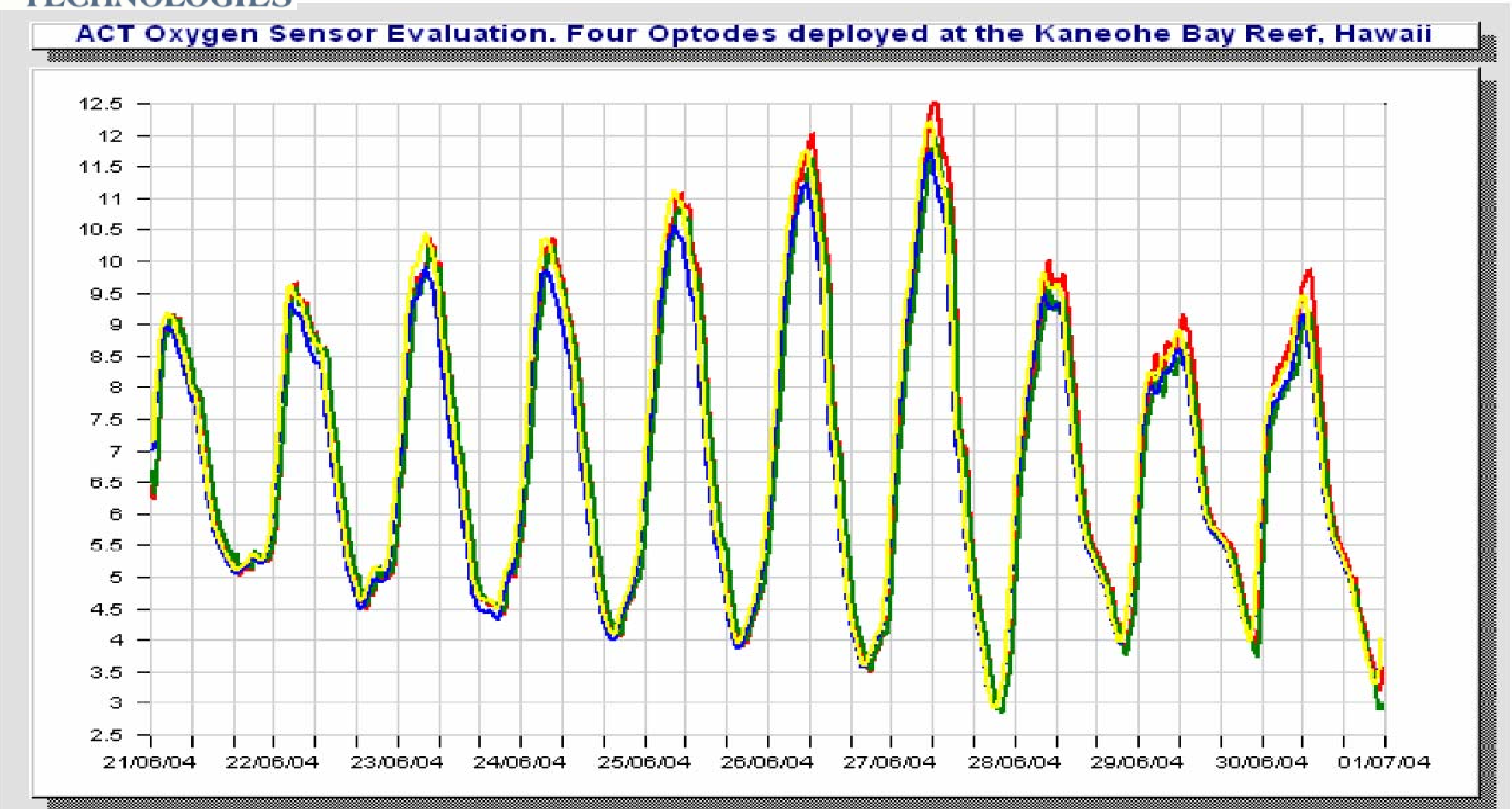

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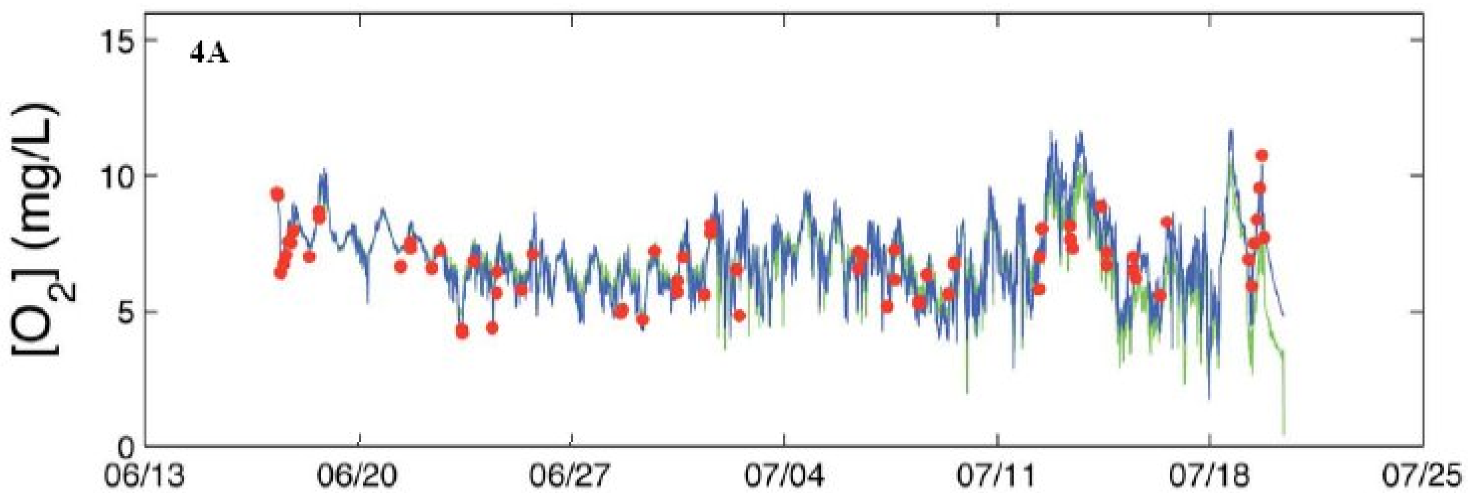
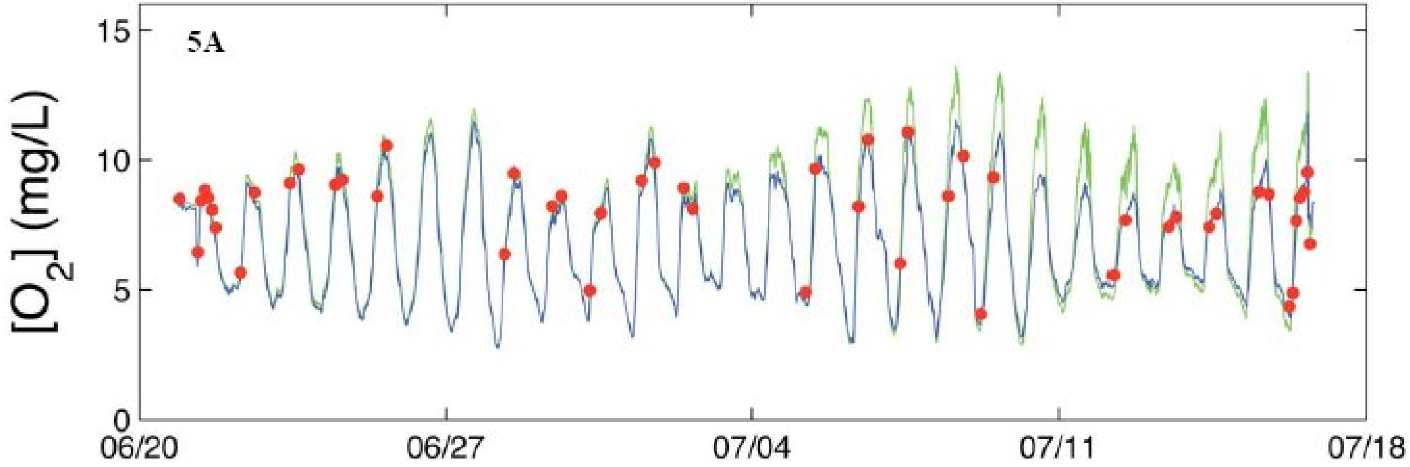
Belleville Lake, MI (University of Michigan) – Fresh water impoundment on the Huron River

Figures 4A and 4B. Instrument drift at Belleville Lake, MI, 4C (CILER/University of Michigan).



Kaneohe Bay Reef, HI (University of Hawaii) – Dynamic coral barrier reef

Figures 5A and 5B. Instrument drift at Kaneohe Bay Reef, HI, 5C (University of Hawaii).



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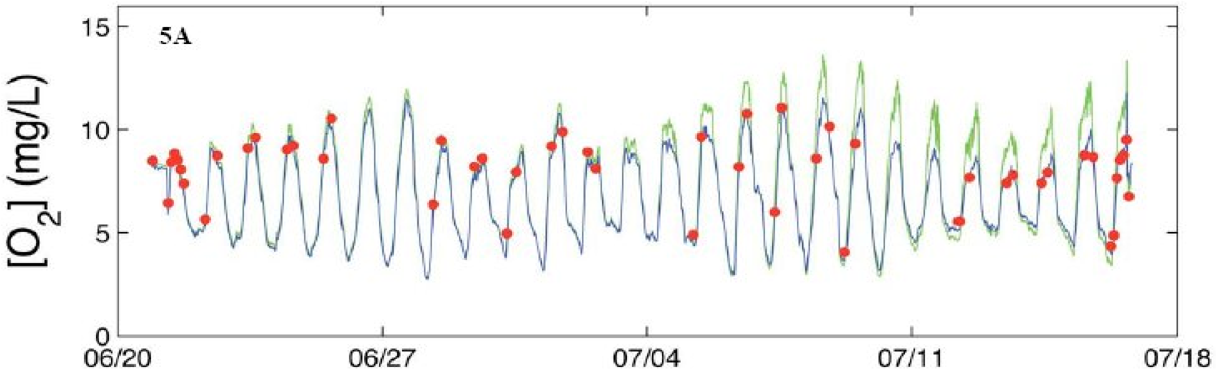
Kaneohe Bay Reef, HI

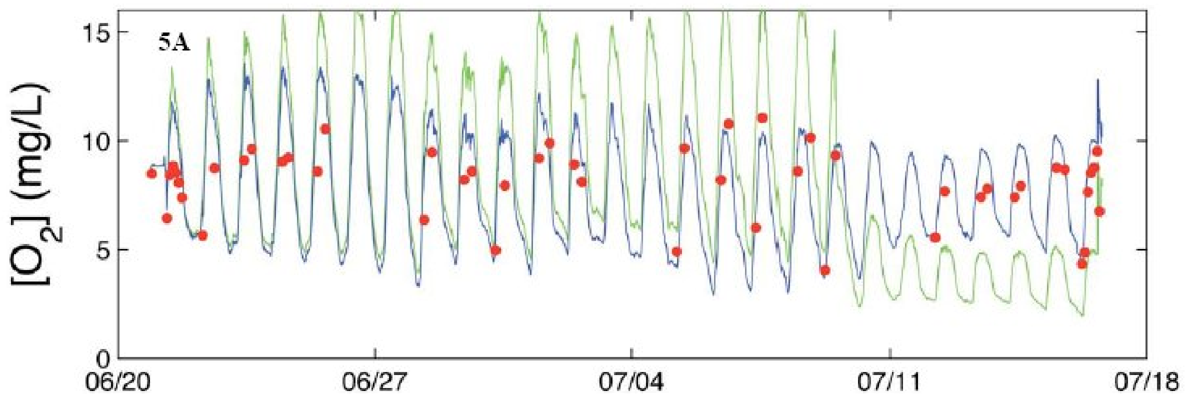
Figures 5A and 5B. Instrument drift at Kaneohe Bay Reef, HI, 5C (University of Hawaii).

Optical DO



Figures 5A and 5B. Instrument drift at Kaneohe Bay Reef, HI, 5C (University of Hawaii).

Polarographic DO



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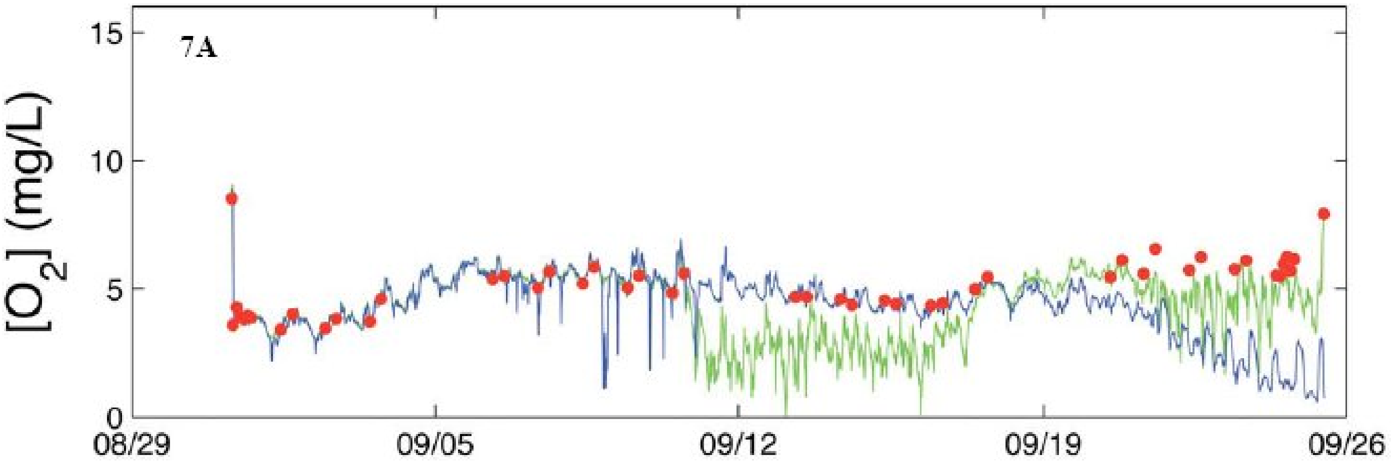
Skidaway Island, GA (Skidaway Institute of Oceanography) – Subtropical estuary on the Skidaway River, western shore of Skidaway Island

Figures 7A and 7B. Instrument drift at Skidaway Island, GA, 7C (SkIO).



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ACT Evaluation – Summary of Results (non-ACT generated table)

Parameter	Winkler Titration	Optical DO	Polarographic	Galvanic
Average Initial Error, mg/L (net bias)	-	**0.19**	**0.55**	0.22
Frequency of Initial Errors 0.2 mg/L or Less	-	**50%**	40%	**10%**
Frequency of Initial Errors 2.0 mg/L or More	-	**0%**	10%	**60%**
Individual Precision	0.22%	**0.11%**	**0.11%**	0.18%
Typical Drift during 1st Week, mg/L	-	**0.39**	0.77	**1.01**
Variability of Drift (worst up – worst down), mg/L	-	**0.58**	**3.94**	0.74
Worst Case # of Days of Good Data before Error exceeds 2.0 mg/L	-	**14**	**3**	10

Green is best in class,

Red is worst in class

- How accurate was it at the beginning?

- Do the instruments match each other?

- How bad was the drift?

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So what's the 'knock' on Optical DO???

- Measurement range limited on high end (200-400% saturation)
- No method approval from EPA for
  - BOD
  - NPDES permit reporting
- New 'unproven' technology?
  - Successful deployments in harsh applications such as:
    - Deep-sea Oceanographic Research >6000 m deep
    - Highly Productive Estuaries
    - Waste Stream Effluents
    - Deep Ground Water Wells
    - Low Temperatures

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So what's the 'knock' on Optical DO???

- Still subject to Biofouling – but even without any biofouling countermeasures can average 2-4 times longer deployments than standard "wiped" DO sensors, especially in highly productive conditions

- Photo bleaching effects if not protected from UV light

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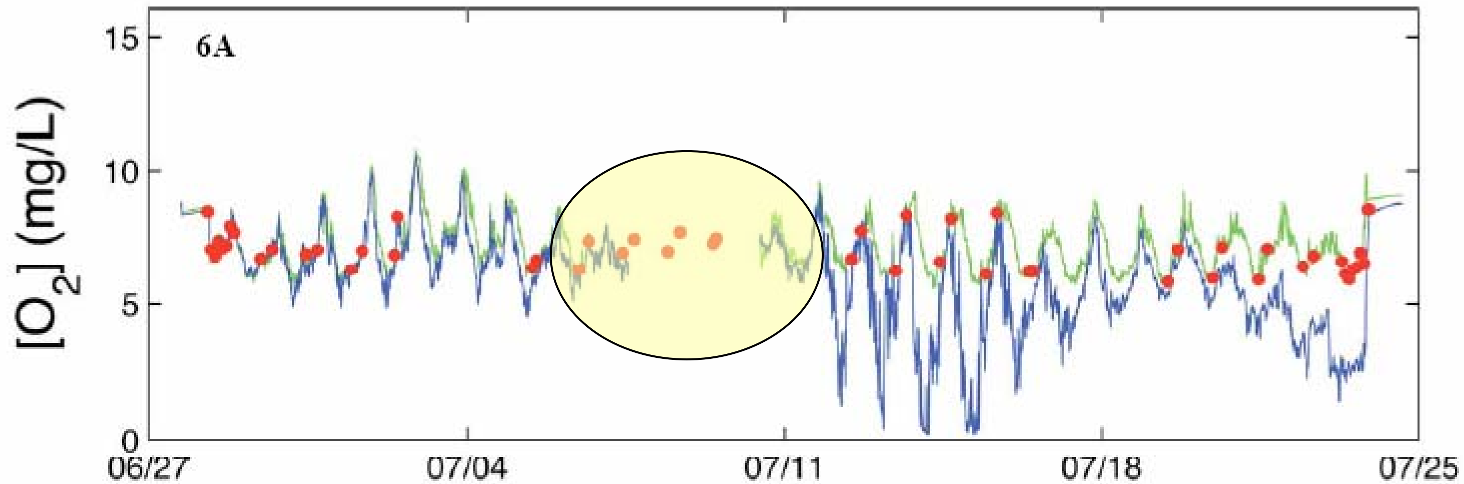
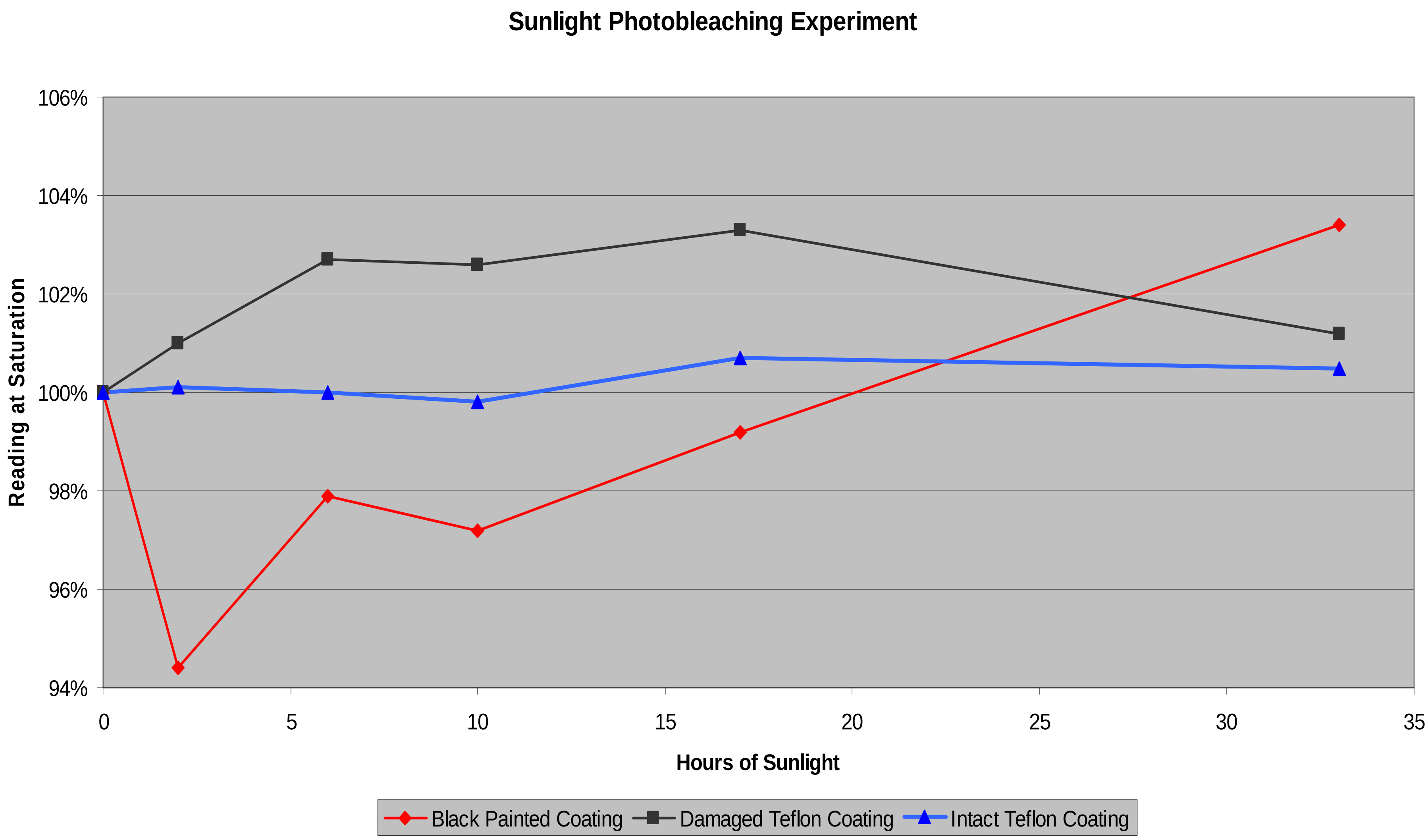
December 1, 2004

Figures 6A and 6B. Instrument drift at Moss Landing, CA, 6C (MLML).



"even though the instruments slipped out of our deployment rack, likely due to the metal housing slickness, and spent 2-3 days in anoxic mud they both continued to record good data and recovered to previous performance levels within 1 sampling interval of return to the surface deployment rack."

Cal State Technical Coordinator



Sunlight Photobleaching Experiment
106%
104%
102%
100%
98%
96%
94%
Reading at Saturation
0
5
10
15
20
25
30
35
Hours of Sunlight
Black Painted Coating
Damaged Teflon Coating
Intact Teflon Coating

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Customer Case Study—can Optical DO save me $$$?

Assumptions

1. Reduce the number of field trips from every 2 weeks to once a month to check instruments and gather data. Vehicle and labor savings

2. Reduction in cost of calibration due to labor and materials.

3. Increase the equipment utilization rate, as equipment does not need to return to the lab for cleaning and recalibration so spare units are not needed

4. Reduction in service expense.

5. Elimination in cost of replacement sensors over lifetime of sonde

Optical DO can reduce cost of ownership by 48% for typical user. RDO also reduces maintenance time, freeing employees for other projects.

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Recap of Optical Dissolved Oxygen Sensors

- No membranes/no electrolyte
- 5 years/5 Million readings before lumiphore is exhausted
- Up to 1 year between calibrations
- Minimal maintenance/no hazardous sensor cleaning solutions
- No sample flow requirements
- Fast and stable response
- Resist biofouling - Suited for long-term deployments
- Little or no sensor drift over several months
- Excellent performance in anoxic conditions—full sensor response at 0 ppm
- Not 'poisoned' by Sulfides
- Accurate results up to and above 200% saturation
- Not subject to 'thermal shocking'
- No cross sensitivity to: H_2S, pH, CO_2, NH_3, SO_4^{2-}, Cl^-, Cl_2, ClO_2, MeOH, EtOH, various ionic species

In Conclusion…

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Q & A